Tracer diffusion in a dislocated lamellar system

Victor Gurarie
Department of Physics, Theoretical Physics, 1 Keble Road, Oxford University, Oxford OX1 1JP, UK

Alexander E. Lobkovsky
Physics Department, Northeastern University, 110 Forsyth Street, Boston, MA 02115
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Many lamellar systems exhibit strongly anisotropic diffusion. When the diffusion across the lamellae is slow, an alternative mechanism for transverse transport becomes important. A tracer particle can propagate in the direction normal to the lamellae, never leaving a particular layer, by going around a screw dislocation. Given the density of positive and negative screw dislocations, we calculate the statistical properties of the transverse transport. When either positive or negative dislocations are in excess, the tracer moves ballistically normally to the layers with the mean square of the displacement growing like the square of time T^2. When the average dislocation charge is zero, the mean square of the normal displacement grows like $T \log T$ for large times. To obtain this result, the trajectory of the tracer must be smoothed over distances of order of the dislocation core size.

Diffusion in layered systems is often strongly anisotropic. The mechanisms and the manifestations of the anisotropy vary. In many such systems diffusion across is significantly slower than along the lamellae. For example, enhanced creep resistance of lamellar alloys, such as industrial TiAl, is probably due to the high barrier for the dislocations crossing from one layer to the next [1, 2]. In lamellar phases of diblock copolymers [3], tracer diffusion along the lamellae can be up to forty times faster than across [4]. The fact that water diffusion in lamellar phases of phospholipid bilayers [5] is strongly anisotropic may be relevant to attempts to use multilamellar vesicles for drug delivery [6]. Another example of anisotropic diffusion is the kinetics of electroactive probes in lyotropic liquid crystals [7].

When lateral diffusion is much faster than transverse diffusion, the tracer can still be transported quickly in the direction normal to the lamellae if screw dislocations are present in the system. A screw dislocation is constructed by cutting a perfect layered structure with a half-plane normal to the layers, shifting the two sides of the cut with respect to each other in the direction normal to the layers by a distance equal to the layer spacing, and finally gluing the cut. Screw dislocations are indeed common in a variety of layered systems [8, 9, 10]. A summary of various dislocation properties in lamellar systems is presented in Ref. [11].

When a tracer particle confined to a particular layer encircles a screw dislocation, it finds itself in one layer higher (or lower). A tracer particle can then reach any point in the system while remaining confined to a layer. The trajectory of the tracer projected onto a plane parallel to the layers is a two-dimensional random walk. Upon completing a closed 2D trajectory, our random walker moves up or down the number of layers equal to the dislocation charge enclosed by the trajectory. We obtain an expression for this quantity by noting that when a single screw dislocation is present in the system, the layer number of the walker is the winding angle around the dislocation divided by 2π. Consider now the sum of the winding angles around all the dislocations (the signs of the individual winding numbers are determined by the charge of the dislocations). This quantity changes continuously. The change in this quantity along an open trajectory depends on the shape of the sample due to the contributions of the winding numbers around distant dislocations. However, when the walker returns to the origin, the change in the total winding number is the dislocation charge enclosed by the trajectory. Thus we identify the total winding number divided by 2π with the layer number $n(t)$ which for closed trajectories coincides with the normal displacement of the walker.

In this letter we study the diffusion of a tracer particle confined to the lamellae. The tracer starts at the origin of layer $n = 0$ at time $t = 0$ and explores the x-y plane with diffusivity D. Let there also be a random distribution of positive and negative screw dislocations with densities f_+ and f_- respectively. Our goal is to determine the nature of the transport normal to the layers by predicting the result of the following experiment. If some amount of the tracer material is placed at the origin at time $t = 0$, what is the density of the resulting cloud of tracer particles as a function of time?

To accomplish this task we look at paths which start at the origin O (see Fig. 1) at time $t = 0$ and arrive to point E located a distance R from the origin at time T. We seek to define the layer number $n(R, T)$. Since the layer number change is only well defined for closed trajectories we fix $n(R, T)$ by completing the path $r(t)$ with a straight segment OE connecting this point to the origin. We can then define $n(R, T)$ to be the total dislocation charge enclosed by this trajectory.

We now seek to average powers of n over positions of dislocations and random walks which end at $r = R$ at

time $t = T$. We denote the average over positions of dislocations with an overbar and average over random walks by angular brackets $\langle\cdot\rangle$. Because changing the shape of the completing segment adds a constant to $n(R,T)$, its average $\langle\,\overline{n}(R,T)\,\rangle$ has no physical meaning. However, its standard deviation $\sigma(R,T) = \left\langle\,\overline{n^2}\,\right\rangle - \langle\,\overline{n}\,\rangle^2$ is independent of the shape of the completing segment. It gives the size of the spreading tracer cloud at time T and distance R from the origin.

We identified two qualitatively different cases.

When $f_+ \neq f_-$, we are able to obtain $\sigma(R,T)$ thereby predicting the tracer density profile within the spreading cloud. This is possible because the average total dislocation charge within a closed trajectory which is proportional to its signed area. In this case we find that the vertical size of the tracer cloud grows linearly in time, i.e. there is superdiffusion across the layers. Moreover, the spreading cloud acquires a biconcave shape, since $\sigma(R,T) \propto D^2T^2 + 2R^2DT$ (here brackets denote averaging over random walks). We must note here that the excess of dislocations of a certain chirality leads in smectics to the break up of the homogeneous lamellar phase into domains separated by twist grain boundaries [12]. We nevertheless pursue this case since it may applicable to the Aharonov-Bohm electron phase fluctuations in a type II superconductor and other systems where geometric winding numbers play a role.

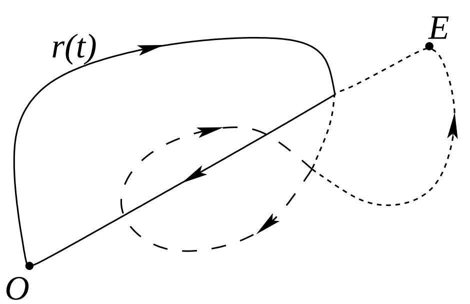

FIG. 1: We complete the path $r(t)$ with a straight segment connecting its beginning O and its end E. The winding angle fluctuation along this closed path can be calculated by decomposing the path into a union of non self-intersecting loops (denoted by the solid, dashed and dotted lines).

When the densities of the positive and negative dislocations are equal, a more subtle averaging must be performed since the average dislocation charge in a closed loop is now zero. We must compute the variance of the dislocation charge within a closed loop. As we discuss below, this variance is proportional to the unsigned area of the loop which has a simple geometrical interpretation.

It turns out that when the dislocations are thought of as point objects, it is not possible to average the unsigned area over random walks. The variance of the layer number obtained in this fashion is logarithmically divergent. Divergences are common in the statistics of winding numbers of random walks [13, 14, 15, 16]. For example, the dispersion of the winding number of a random walker around a point is divergent if the walk is continuous. This divergence arises due to the contributions to the winding number from trajectories which wind tightly around the point. The nature of our divergence is similar. By traversing a short distance around a dislocation a tracer particle travels far in the direction normal to the layers, and that leads to the anomalously fast diffusion in the direction perpendicular to the layers.

We regularize this divergence by noting that the core size a determines the distance of the closest approach of the tracer to the dislocations. Therefore small loops in the trajectory are irrelevant for our purposes. We should therefore look at an effective discrete random walk whose steps are of length a taken every a^2/D seconds. We then are able to calculate the variance of the layer number which grows as $\sigma(R,T) \propto T\log T$. Since $\sigma(R,T)$ is independent of R,, the shape of a spreading cloud in this case is an ellipsoid which elongates in the direction normal to the layers. Note also that this divergence would have appeared in the case of different densities of positive and negative dislocations. It leads to a correction of order $T\log T$.

We now describe our methods and results in more detail. Let $r_\alpha(t)$ be the Brownian trajectory of the tracer (here α is the two dimensional vector index). We take its velocity $\dot{r}_\alpha(t)$ to be random and white noise correlated in time, neglecting possible correlations on time scales of the order of the scattering time of the walker, which is much smaller than all other time scales in our problems.

$$\langle\,\dot{r}_\alpha(t)\dot{r}_\beta(t')\,\rangle = \delta_{\alpha\beta}\left[\frac{D}{2}\left(\delta(t-t') - \frac{1}{T}\right) + \frac{R_\alpha^2}{T^2}\right]. \quad (1)$$

Eq. (1) involves constant terms in addition to the standard $\delta(t-t')$ one. This is because averaging in Eq. (1) is done with the boundary conditions $r(0) = 0$, $r_\alpha(T) = R_\alpha$, needed to compute the layer number n as a function of position R and time T.

Dislocations of charge q_i are located at x^i_α. q_i takes on values ± 1. The layer number $n(R,T)$ can be expressed in the following way

$$n(R,T) = \sum_i \frac{q_i}{2\pi}\int dt\, \frac{\epsilon_{\alpha\beta}\dot{r}_\beta\left(r_\alpha - x^i_\alpha\right)}{|r - x^i|^2}, \quad (2)$$

where $\epsilon_{\alpha\beta}$ is the antisymmetric tensor of rank 2. Indeed, the expression to be integrated over time in Eq. (2) is just the sum over all the dislocations of the infinitesimal change of the angle between the x-axis and the vector connecting the tracer particle and the dislocation. Thus (2) is the cumulative winding number of the tracer around the dislocations. According to the preceding discussion (see Fig. 1), the function $r(t)$ in (2) consists of two segments. The first is a Brownian walk from $t = 0$

to time T. The second is a straight line from $r(T) = R$ back to the origin.

Since we are interested in the statistical properties of $n(R,T)$, expression (2) must be first averaged over dislocation strengths q_i and positions x_i and then over Brownian trajectories $r(t)$. To perform the averaging, we assume that positive and negative dislocations are distributed uniformly. If the total density is $f = f_+ + f_-$, the dislocation strength is $q_i = 1$ with probability f_+/f, and $q_i = -1$ with probability f_-/f.

Averaging (2) over the strengths and positions of the dislocations we arrive at

$$\overline{n}(R,T) = (f_+ - f_-) \int dt \, \frac{\epsilon_{\alpha\beta}}{2} \, r_\alpha \dot{r}_\beta. \tag{3}$$

The integral in (3) can be interpreted geometrically as the overall area covered by a vector connecting the tracer particle to the origin as the particle moves along its trajectory. The area is computed with the sign, so that when the vector rotates clockwise, the area it covers is added, while when it moves counterclockwise, it is subtracted from the answer. We refer to the integral in (3) as the signed area.

Eq. (3) has a simple intuitive interpretation. If the densities of the positive and negative dislocations were the same, we would expect $\overline{n}(R,T)$ to vanish, because on average the tracer would encircle an equal number of positive and negative dislocations. The signed area times the difference in the dislocation densities is on average precisely the overall number of dislocations encircled clockwise minus the overall number of dislocations encircled counterclockwise, which should give $\overline{n}(R,T)$.

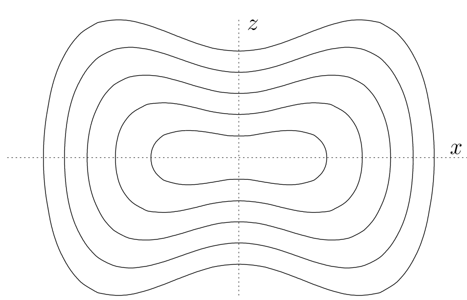

FIG. 2: Five equidistant in time snapshots of the isodensity line of the vertical slice through the expanding tracer cloud when $f_- \neq f_+$. The cloud's shape is a figure of revolution of this slice around the z-axis. The lines are drawn at the level where the density is equal 0.1 of the maximum density in the center of the cloud. Note that that cloud develops into a biconcave shape elongated in the vertical direction (normal to the layers).

At this point, we must clearly distinguish between the $f_- = f_+$ and $f_- \neq f_+$ cases. If the difference in dislocation densities is zero, then $\overline{n}(R,T)$ computed in this way is zero and we must take into account the fluctuations in the total dislocation charge enclosed by a trajectory. Let us first concentrate on the case $f_- \neq f_+$.

With these preparations, it is now straightforward to average powers of $\overline{n}(R,T)$ over the Brownian walks, with the help of (1). The average $\langle \overline{n} \rangle$ of (3) can be shown to be zero, owing to the straight shape of the completing segment OE of Fig. 1. The standard deviation $\sigma(R,T)$ can then be computed as $\overline{n^2}(R,T)$. However we can neglect the difference $\left\langle \overline{n^2} \right\rangle - \left\langle \overline{n}^2 \right\rangle$ which can be shown to grow slower in time than $\sigma(R,T)$. We obtain

$$\sigma(R,T) \approx \left\langle \overline{n}^2 \right\rangle = \frac{(f_+ - f_-)^2}{48} \left(D^2 T^2 + 2R^2 DT \right). \tag{4}$$

This is the first of the two main results of this letter. Noting that $\left\langle R^2 \right\rangle = DT$ for a Brownian walker, we conclude that the tracer particle indeed moves superdiffusively in the normal direction. Furthermore, (4) gives us a way to calculate the approximate shape of a tracer cloud shown in Fig. 2.

Moreover, it is also possible to compute the entire probability distribution of $\overline{n}(R,T)$ which allows us to determine the density of the cloud. This calculation involves averaging the exponential of (3) over the Brownian walks using Gaussian functional integral techniques. The answer, given in terms of infinite products, is not illuminating. We only note here that the probability distribution $P(\overline{n},T)$ of a simpler quantity $\overline{n}(T)$, which is the average of $\overline{n}(R,T)$ over all positions R, can be calculated in closed form,

$$P(\overline{n},T) = \frac{2}{|f_+ - f_-| \, DT} \left[\cosh\left(\frac{2\pi \overline{n}}{(f_+ - f_-)\, DT} \right) \right]^{-1}. \tag{5}$$

The situation becomes more interesting when $f_- = f_+$. In this case, to compute $\overline{n^2}$ we need to square (2) first and then average over positions and strengths of dislocations. We obtain

$$\overline{n^2}(R,T) = -\frac{f}{4\pi} \int dt \int dt' \; \dot{r}_\alpha(t)\, \dot{r}_\beta(t') \; G_{\alpha\beta}(r(t) - r(t')), \tag{6}$$

where $G_{\alpha\beta}(r) = \delta_{\alpha\beta} \log(r) - \frac{r_\alpha r_\beta}{r^2}$ is often referred to as the 2D photon propagator. This formula represents the unsigned area of the loop formed by $r(t)$. It was used in [17] to compute areas formed by loops in a different context.

There is an intuitive way to understand why the unsigned area appears in this context. It can be computed geometrically as follows. First decompose a self-intersecting loop into a union of non self-intersecting subloops (see Fig. 1). We can then show that the variance of the dislocation charge enclosed by the loop is equal to the sum of the unsigned areas of the subloops plus the sum over all pairs of subloops of the areas of their intersections with a plus sign if the two subloops are traversed in the same direction and with the minus sign if they are traversed in opposite directions.

To simplify the task of averaging (6) over Brownian walks, we follow the example of Ref. [17] and rewrite the photon propagator in the following equivalent way

$$\overline{n^2}(R,T) = -\frac{f}{2}\int dt \int dt'\, \dot{r}_1(t)\, \dot{r}_1(t')\times \\ \delta(r_1(t) - r_1(t'))\ |r_2(t) - r_2(t')|. \quad (7)$$

The advantage of this formula over (6) is in the fact that r_1 and r_2 coordinates of the 2D Brownian walker decouple and become two independent 1D Brownian walks.

It turns out that the average of (7) over random walks is logarithmically divergent at $t \approx t'$. Anticipating that, we only need to average (7) at $t \to t'$. That means, we can neglect all the terms in (1) which depend on T and R_α, while keeping only the $\delta(t - t')$ term. We obtain

$$\langle\, |r_2(t) - r_2(t')|\, \rangle \approx \sqrt{\frac{2D|t-t'|}{\pi}}, \quad (8)$$

and

$$\langle\, \dot{r}_1(t)\dot{r}_1(t')\, \delta\left(r_1(t) - r_1(t')\right) \rangle \approx \\ \sqrt{\frac{D}{2\pi\, |t-t'|}}\left[\delta(t-t') - \frac{1}{4|t-t'|}\right]. \quad (9)$$

Substituting this into (7) we find the leading term

$$\sigma(R,T) = \left\langle \overline{n^2}(R,T) \right\rangle = \frac{fD}{8\pi}\int dt \int dt'\ \frac{1}{|t-t'|}. \quad (10)$$

It is clear that the $t = t'$ divergence in (10) should be regularized to give

$$\sigma(R,T) = \frac{fDT}{8\pi}\log\left(\frac{T}{\epsilon}\right). \quad (11)$$

The regulator ϵ appears due to the fact that the trajectory cannot wind around a given dislocation tighter than the dislocation core size a. The continuous formula (6) breaks down at distances smaller than a. The length a corresponds to time interval $\epsilon = a^2/D$ which is the average time it takes the random walker to diffuse across a dislocation core. We obtain

$$\sigma(R,T) = \frac{fDT}{8\pi}\log\left(\frac{DT}{a^2}\right). \quad (12)$$

This is the second main result of this letter. Notice that $\sigma(R,T)$ does not depend on R, which should be contrasted with (4) which is valid when $f_+ \neq f_-$.

To summarize, we considered tracer diffusion in a layered system with screw dislocations. When the transverse diffusion coefficient of the is small compared to the in-plane diffusion coefficient, tracer particles are transported in the direction normal to the layers by encircling screw dislocations. We predict the shape of a cloud of the tracer particles as a function of time. We find that size of the cloud in the direction normal to the layers (its height) grows faster than its width.

To make quantitative predictions we need to address the following concern. The conventional transverse tracer diffusion coefficient $D_\perp$ is never identically zero. Tracer particles can be transported along dislocation cores or point defects such as pores, necks and passages as suggested by Constantin and Oswald in [18]. They measured transverse diffusion in a thin sample of lamellar phase of a surfactant/water mix. Since their sample contained only a few dislocations across its thickness, our effect would therefore not be operative. Instead one can estimate the effect of an isolated screw dislocation using the classic result of the statistics of winding numbers (e.g. [15]) to be negligible compared with conventional diffusion $D_\perp$.

Going back to a layered system with many screw dislocations, we need to estimate the time after which the superdiffusion due to dislocations will dominate conventional transverse diffusion. We consider the case of equal densities of positive and negative dislocations because unless there is a process at work which selects dislocations of a certain charge, the difference in the densities will be small. The height of the cloud due to conventional diffusion is roughly equal to the height due to superdiffusion when

$$D_\perp T \sim d^2 f DT \ln\frac{DT}{a^2}, \quad (13)$$

where d is the interlayer distance. Assuming that the dislocation core size is equal to the interlayer spacing we obtain the crossover time

$$T_{\rm c} \sim \frac{d^2}{D}\, \exp\left(\frac{D_\perp/D}{d^2 f}\right). \quad (14)$$

If this time is comparable to the experimentally available time, our phenomenon should be observable.

Ref. [4] measured the anisotropy of the diffusion coefficient in clean samples of diblock copolymer to be $D_\perp/D \approx 10^{-2}$. Therefore, in order for our effect to manifest itself, the defect density must be two orders of magnitude larger than $d^2 f \approx 10^{-5}$ observed in the shear aligned diblock copolymer system of Ref. [4]. The diffusion of water mixed with egg phosphatidylcholine [5] is even more anisotropic $D_\perp/D \approx 10^{-3}$ so that our effect can be observed for smaller defect densities. A promising system is a mixture of lipid and surfactant which undergoes a lamellar to nematic transition via proliferation of screw dislocations [9, 18].

To conclude we mention two phenomena which require a modification of our predictions. First, if screw dislocations are mobile, they will tend to form bound dipole pairs of size comparable to the core size. Since the bound pairs do not contribute to the transverse transport of the tracer, only the density of free dislocations must be used in Eq. (12). In addition, the dislocation motion [11, 19]

will lead to an additional mechanism for normal transport of the tracer. Second, the presence of edge dislocations impedes in-plane diffusion of the tracer. This fact may be successfully taken into account by renormalizing the in-plane diffusivity.

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